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Electrochemical techniques applied to studies of microbiologically influenced corrosion(MIC)

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ABSTRACT

Electrochemical techniques including measurements of corrosion potential, redox potential, polarization resistance, electrochemical impedance, electrochemical noise, polarization curves, and electrochemical hydrogen permeation techniques have been applied to studies of microbiologically influenced corrosion (MIC). Applications include evaluation of MIC of metals exposed to seawater, fresh water, demineralized water, process chemicals, food stuffs, soils, aircraft fuels, human plasma, and sewage. In this review electrochemical data from laboratory and field applications are presented and interpreted in terms of mechanisms of MIC.

INTRODUCTION

MIC is due to the activities of microorganisms on metal surfaces which may lead to changes in rates and/or types of electrochemical reactions involved in corrosion processes. Corrosion rates might be increased because of an increase of the rate of anodic and/or cathodic partial reactions involved in the corrosion process without a change of the corrosion mechanism. It is also possible that the nature of the corrosion process is changed and a different reaction mechanism occurs in the presence of microorganisms. Evidence for a shift in the corrosion process as a result of microbial activity can be found in MIC due to sulfate-reducing bacteria (SRB), where it has been suggested that in the absence of oxygen (anaerobic conditions) the cathodic reaction involves reduction of H_2S produced by bacteria (Costello, 1974; Tiller, 1986; Hamilton, 1990) according to:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2 . \qquad (1)$$

Further evaluation of this mechanism shows (King

and Miller, 1981; Hamilton, 1990) that the major factor governing the corrosion rate under these conditions is the formation of FeS:

$$Fe + S^{2-} \rightarrow FeS + 2e^- . \qquad (2)$$

This brief discussion demonstrates that bacteria can change the mechanism of corrosion from that commonly observed in abiotic environments. It is therefore important to focus electrochemical investigations not only on the determination of the acceleration of corrosion rates, but also on mechanistic aspects of MIC.

The presence of microorganisms on metal surfaces often results in highly localized changes of the concentration of electrolyte constituents, pH and oxygen levels (Gerchakov et al., 1986; Little et al., 1990a). Since such changes can lead to localized corrosion of passive metals in the form of pitting or crevice corrosion, it is necessary in electrochemical studies of MIC to employ techniques which are especially suited for the evaluation of localized corrosion phenomena.

Electrochemical techniques are useful for mechanistic studies in laboratory investigations and for monitoring purposes in field studies. As with all studies of corrosion phenomena, more detailed and reliable information can be obtained when a number of different electrochemical techniques are combined. In the case of MIC, additional information from microbiological and surface analytical techniques such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS) is required for the interpretation of electrochemical phenomena. This review will focus on the use of electrochemical techniques in investigations of MIC and interpretation of information

obtained with these techniques.

This review is an update of an earlier literature review (Mansfeld and Little, 1990a and b; Mansfeld and Little, 1991a) including recent papers and the information available in the Proceedings of the International Congress on Microbially Influenced Corrosion and Biodeterioration held in October 1990.

ELECTROCHEMICAL TECHNIQUES

Corrosion Potential

Measurement of the corrosion potential (E_{corr}) is the easiest electrochemical test to perform, but it provides the least amount of mechanistic information. The main problem with the use of independent E_{corr} measurements is the overinterpretation of the data. E_{corr} alone cannot be used to determine whether corrosion rates have increased or decreased. If polarization resistance (R_p) is measured at the same time as E_{corr}, then changes in both parameters can be interpreted based on mixed potential theory in terms of changes in the rates of anodic and/or cathodic partial reactions which determine the corrosion rate.

Early measurements of E_{corr} for carbon steel in the presence of SRB suffer from lack of additional information and are therefore difficult to interpret. Shifts in E_{corr} in the negative direction have been explained by a reduction of the rate of the cathodic reaction (Hadley, 1943) and/or by an increase of the rate of the anodic reaction (Wanklin and Spruit, 1952). Without additional data, valid conclusions concerning the effect of SRB on electrochemical corrosion reactions cannot be drawn. Only when the exact mechanism of MIC has been established for a given system, is it possible to use E_{corr} data to detect an increase of uniform corrosion rates or the initiation of localized corrosion due to the presence of bacteria.

The time dependence of E_{corr} has been monitored for stainless steels (SS) in natural seawater by many investigators. Most published data show a rapid ennoblement of E_{corr} during the early stages of exposure (Mollica et al., 1984; Scotto et al., 1985; Johnsen and Bardal, 1985; Johnsen and Bardal, 1986; Videla et al., 1987; Mollica et al., 1988; Dexter and Gao, 1988; Mollica et al., 1989). Figure 1 shows potential-time curves reported by Johnsen and Bardal (1985) for several stainless steels in flowing (0.5 m/s) natural seawater. E_{corr} changed from –200 mV to –250 mV (SCE) at the beginning of the test to –50 mV for two of the alloys and to +200 mV for the remaining four alloys after 28 days. Ennoblement of E_{corr} was attributed to a change of the cathodic properties of the stainless steels as a result of microbiological activity on the surface. Mollica et al.
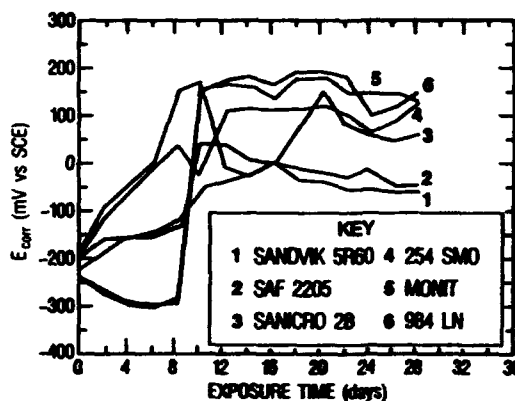

Figure 1. Open-circuit potential vs. time for six stainless steels exposed to flowing natural seawater (Johnsen and Bardal, 1985).

(1990) recently conducted field tests for stainless steels using E_{corr} in conjunction with electrochemical impedance spectroscopy (EIS) and rate of oxygen reduction at constant potential. They concluded that a mechanism involving the absorption of some "chemical" produced by bacteria that acts as a catalyst for the oxygen reduction reaction, and whose efficiency increases as the surface pH exceeds the value of 8, was the most probable explanation of ennoblement of E_{corr}.

Dexter and Gao (1988) reported E_{corr} data and polarization curves for SS316 exposed to natural seawater and concluded that the observed scatter of the E_{corr} data in seawater was due to the presence of microorganisms. However, in a subsequent discussion of these data (Mansfeld and Little, 1989), it became apparent that extreme negative E_{corr} values for some of the samples were due to crevice corrosion under a lacquer. Based on results obtained with cathodic polarization curves, Dexter and Gao (1988) concluded that increase of E_{corr} for remaining samples of SS316 was due to an increased rate of the cathodic reduction of oxygen. It is commonly assumed that as E_{corr} increases and approaches the pitting potential, the probability of localized corrosion increases. However, results of several authors reporting an ennoblement of E_{corr} for stainless steels during exposure to natural seawater do not demonstrate directly an increased susceptibility to localized corrosion. In fact, sustained noble potentials indicate that the stainless steels retained their normal corrosion

resistance in seawater for the duration of the experiments. If localized corrosion had occurred in these experiments, E_{corr} would have dropped to the active potentials typical of pitted stainless steels.

It is not possible from E_{corr} measurements or the polarization curves to decide whether the increase of the rate from the cathodic reaction which leads to the observed ennoblement of E_{corr} is due to thermodynamic effects, kinetic effects, or both. The reversible potential of the oxygen reduction reaction $E°_{O_2/OH^-}$ can increase due to a local increase of the oxygen concentration p_{O_2} or a decrease of pH. However, an increase of p_{O_2} has only a small effect on $E°_{O_2/OH^-}$, while local acidification would reduce the pitting potential below the observed values of E_{corr}. The complexity of this situation is illustrated by the fact that naturally-occurring microorganisms within a marine biofilm can decrease or increase the local oxygen concentration and/or pH. Little et al. (1990a) and Lewandowski et al. (1989) reported some of the first measurements of the biofilm/metal interfacial chemistry and demonstrated the impact of interfacial chemistry on the development of E_{corr} with exposure time. An increase of the exchange current density for the oxygen reduction reaction would also lead to an increase of E_{corr}. Since E_{corr} is a mixed potential, its value can also change in response to changes in the passive current density of the stainless steel. At constant kinetics of the oxygen reduction reaction, E_{corr} will become more noble if the passive current density decreases with exposure time. Despite all the attention which the ennoblement of E_{corr} of stainless steels has received, no valid mechanism for the increase of the rate of oxygen reduction reaction during formation of the biofilm, which is the cause of the ennoblement, has been confirmed.

Little et al. (1990b) and Mansfeld et al. (1990a, 1991b) demonstrated that details of the exposure conditions can have pronounced effects on the constituents of the biofilm, interfacial chemistry, and the resulting E_{corr}. In exposure to flowing natural Pacific Ocean water, they found that E_{corr} for three stainless steels and titanium did not change significantly over a period of four months (Fig. 2). Laboratory tests for the same materials in abiotic media (NaCl and artificial seawater) produced similar results (Mansfeld et al., 1989).

E_{corr} data have also been reported for mild steel (buried pipes) in the presence of SRB (Kasahara and Kajiyama, 1986; King et al., 1986; Smorodin et al., 1986). Kasahara and Kajiyama (1986) used a combination of E_{corr}, linear polarization, and impedance data for monitoring purposes. E_{corr} values have also been used in the evaluation of corrosion problems caused by fungal attack of aluminum alloys used as
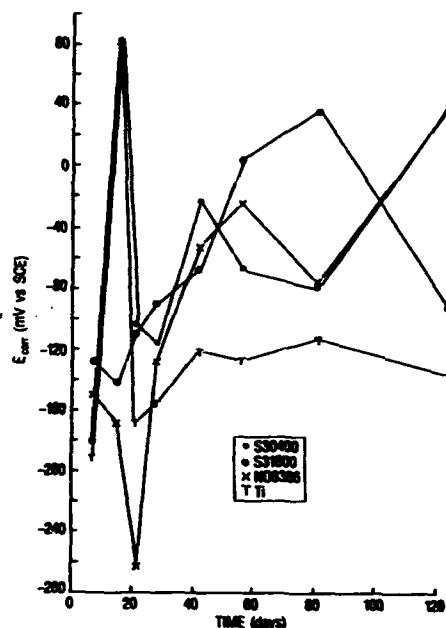

Figure 2. Open-circuit potential vs. time for three stainless steels and titanium exposed to flowing natural seawater (Mansfeld et al., 1990a, 1991b).

tanks for aircraft fuel (Salvarezza et al., 1983).

Redox Potential

The reduction-oxidation (redox) or solution potential is usually measured on an inert electrode such as platinum. Redox potential is an indicator of the oxidation power of the electrolyte and could be used as an indicator of the corrosivity of the electrolyte if suitable calibration were provided. Redox potentials have been used to monitor changes in the corrosive properties of solutions as a result of bacterial metabolism. However, exposure to a solution of a given corrosivity, i.e., redox potential, can produce varying degrees of corrosion for different metals. For the assessment of potential problems with MIC in soils, the redox potential, in combination with soil conductivity and water content, has provided useful information (Booth, 1971).

Polarization Resistance

The polarization resistance technique can be used to continuously monitor the instantaneous corrosion rate of a metal. A thorough review of the use of

polarization resistance techniques for the measurement of corrosion currents has been given by Mansfeld (1976). R_p is defined as the slope of a potential (E)-current density (i) curve at E_{corr}, where i = 0:

$$R_p = (dE/di)_{i=0}.$$ (3)

The corrosion current density (i_{corr}) is calculated from R_p by:

$$i_{corr} = B/R_p,$$ (4a)

where

$$B = b_a b_c/2.303 \ (b_a + b_c).$$ (4b)

The exact calculation of i_{corr} requires simultaneous measurements of R_p and Tafel slopes (b_a and b_c). Computer programs such as CORFIT (Mansfeld, 1973a), POLCURR (Gerchakov et al., 1981), and POLFIT (Shih and Mansfeld, 1990) have been developed for the determination of precise values of i_{corr} according to Equation 4a and b. For localized corrosion, the experimental R_p data should be used only as a qualitative indication that rapid corrosion is occurring. Large fluctuations of the R_p data with time are often observed for systems undergoing pitting or crevice corrosion.

A simplification of the polarization resistance technique is the linear polarization technique (Stern and Geary, 1957; Mansfeld, 1976) in which it is assumed that the relationship between E and i is linear in a narrow range around E_{corr}. Usually only two (E, i) points are measured and B is assumed to have a constant value of about 20 mV. This approach is used in field tests and forms the basis of commercial corrosion rate monitors. R_p can also be determined as the dc limit of the electrochemical impedance.

Applications of the polarization resistance technique have been reported by King et al. (1986) in a study of the corrosion behavior of iron pipes in environments containing SRB. In a similar study, Kasahara and Kajiyama (1986) used R_p measurements with compensation of the ohmic drop and reported results for active and inactive SRB conditions. Nivens et al. (1986) calculated i_{corr} from experimental R_p data and Tafel slopes for SS304 exposed to a seawater medium containing the non-sulfate-reducing bacterium *Vibrio natriegens.*

Little and Mansfeld (1991) determined Tafel slopes and i_{corr} from polarization curves obtained within +/- 30 mV from E_{corr} for rotating cylinder electrodes (RCE) of five copper-based materials exposed to natural flowing Pacific Ocean water and artificial seawater to determine the effects of biofilm and
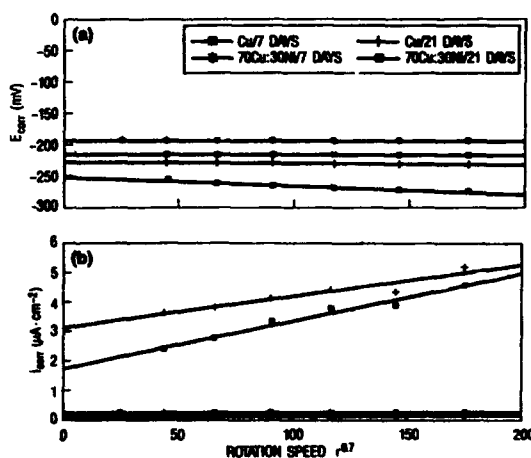

Figure 3. Dependence of (a) E_{corr} and (b) i_{corr} on rotation speed $r^{0.7}$ for 99Cu and 70Cu:30Ni exposed to natural seawater for 7 and 21 days (Mansfeld et al., 1991c).

corrosion product formation on corrosion kinetics and to evaluate the influence of mass transport on anodic and cathodic reactions. Polarization curves were obtained for 99Cu, 90Cu:10Ni, 70Cu:30Ni, admiralty brass, and aluminum bronze as a function of rotation speed and exposure time and analyzed using POLFIT (Shih and Mansfeld, 1990). Figure 3 shows the dependence of E_{corr} (Fig. 3a) and i_{corr} (Fig. 3b) on $r^{0.7}$, where r is the rotation speed of the RCE in rpm, for 99Cu and 70Cu:30Ni after exposure for 7 and 21 days to natural seawater. Similar results were obtained for the other three materials and all exposure times. The independence of E_{corr} on r and the increase of i_{corr} with r for all materials except 70Cu:30Ni suggests that the anodic reaction is under mixed charge and mass transport control. This conclusion is confirmed by the experimental values of the anodic Tafel slope of about 60 mV (Little and Mansfeld, 1991).

The dependence of E_{corr}, i_{corr}, b_a and b_c on r can be expressed in the general form (Little et al., 1991):

$$y_i = y^o_i + b_i r^{0.7}.$$ (5)

By extrapolation to r = 0, y^o_i values for stagnant conditions can be determined. Figure 4 shows the time dependence of i^o_{corr} for the copper-containing five materials for an exposure period exceeding two months. Corrosion rates showed a gradual decrease
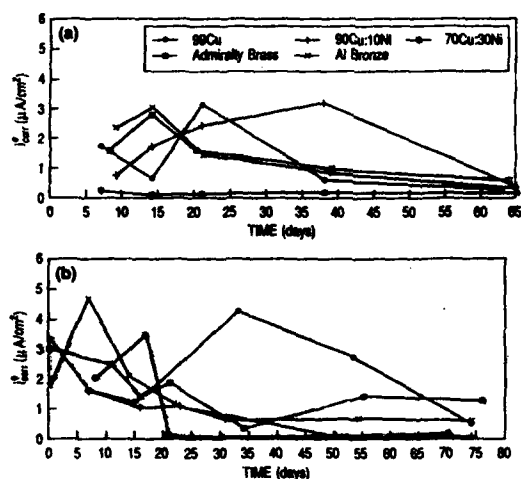
Figure 4. Time dependence of i°_{corr} for five copper-based materials exposed to (a) natural and (b) artificial seawater (Mansfeld et al., 1991a).

with time and had comparable values in both natural and artificial seawater. Similar results have been obtained for E°_{corr}, b°_a and b°_c (Mansfeld et al., 1991b). No significant changes of the corrosion mechanism as expressed by the values of the Tafel slopes were observed during the formation of corrosion product layers and biofilms in natural seawater.

Mansfeld et al. (1990b, 1991a) used the linear polarization technique to determine R_p for mild steel sensors embedded in concrete during exposure to a sewer environment for about nine months. One sample was periodically flushed with sewage in an attempt to remove the acidic environment produced by sulfur oxidizing bacteria (SOB) with a biofilm. SOB convert H_2S, produced by SRB in the sewage, to H_2SO_4 on the crown of the sewer pipe. Another sample was used as a control. A data logging system collected R_p at 10 min intervals simultaneously for the two corrosion sensors and two pH electrodes placed at the concrete surface. Figure 5 shows the cumulative corrosion loss Σ INT obtained by integration of $1/R_p$ vs. time curves as:

$$\Sigma \text{ INT} = \int dt/R_p . \qquad (6)$$

The integrated corrosion loss Σ INT is given in units of sec/ohm. A qualitative measure of the corro-
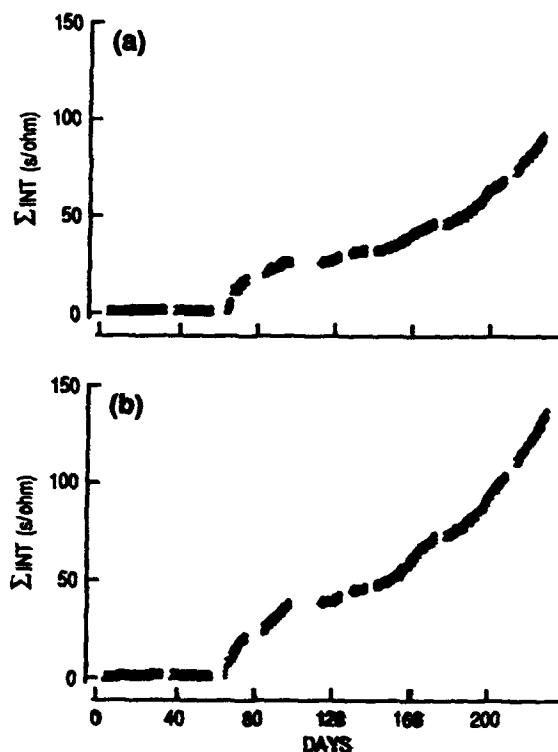

Figure 5. Cumulative corrosion loss Σ INT for mild steel sensors embedded in concrete and exposed to a sewer bypass. (a) Control sample and (b) flushed sample (Mansfeld et al., 1990b, 1991a).

sion rate can be obtained from the slope of the curves in Figure 5. Due to the presence of the uncompensated ohmic resistance in the concrete and the lack of experimental Tafel slopes, the data in Figure 5 have to be viewed as a qualitative measure of changes in corrosion rates. Corrosion loss remained low during the first two months followed by a large increase for both samples when the surface pH reached values of 1 or less. Total corrosion loss as determined from integrated R_p data was less for the control than for the flushed sample.

Dual-Cell Technique

The dual-cell or split-cell technique developed by Little et al. (1986) and Gerchakov et al. (1986) for the study of MIC allows continuous monitoring of

changes in the corrosion rate of a metal due to the presence of a biofilm. In this technique two identical electrochemical cells are biologically separated by a semipermeable membrane. Bacteria are added to one of the two cells. The two working electrodes are connected to a zero resistance ammeter (ZRA) or a potentiostat set to an applied potential of 0 mV. The resulting galvanic current provides a continuous record of the time dependence of the changes of corrosion rates due to the presence of bacteria. The sign and the magnitude of the galvanic current can be used to determine details of the corrosive action of bacteria. The galvanic current is a measure of the increase of the corrosion current of the anode due to the coupling to the cathode and does not allow quantitative calculation of the corrosion rate of either electrode in a simple manner (Mansfeld, 1973b). Applications of the dual-cell techniques have been reported by Little and Wagner (1986), Wagner and Little (1986), and Little et al. (1986).

Daumas et al. (1988) used a dual-cell termed a "biological battery" to study the corrosion mechanism of mild steel in the presence of hydrogenase-containing (Hase$^+$) and non-hydrogenase (Hase$^-$) SRB. Figure 6 shows the galvanic current density between a sterile cell and an inoculated cell in the presence of Hase$^-$ SRB (curve A) and in the presence of Hase$^+$ SRB (curve B). The authors concluded that the oxidation of cathodic hydrogen by bacteria was the dominant corrosion mechanism for Hase$^+$ organisms and suggested that FeS plays an important role in the corrosion reaction with Hase$^-$ organisms. Webster et al. (1990)

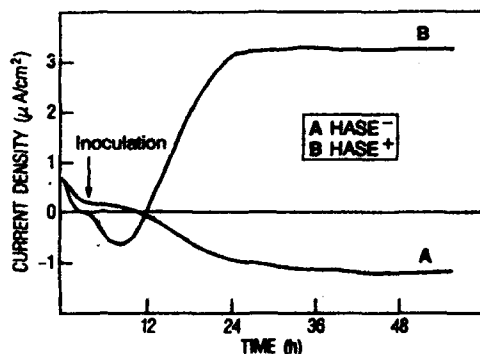used a dual-cell to evaluate localized corrosion of a chromium-depleted steel (Fe:15Cr:10Ni) in media containing SRB.

Electrochemical Impedance Spectroscopy (EIS)

EIS techniques record impedance data as a function of the frequency of an applied signal at a fixed working point (E, i) on a polarization curve (Mansfeld and Lorenz, 1991). In most corrosion studies, this working point is the corrosion potential (E = E_{corr}, i = 0). A large frequency range must be investigated to obtain the complete impedance spectrum, typically ranging from 65 kHz—the upper limit of commonly used frequency response analyzers—to about 1 mHz. Impedance data are usually determined with a three-electrode system, although it is possible to use a two-electrode system where both electrodes are of the same material.

Information obtained with EIS differs from that determined with other techniques described in this review. For EIS measurements the corrosion system is analyzed at a fixed potential (or current density). The properties of the system at this potential can then be determined through the analysis of the frequency dependence of the impedance. One of the advantages of EIS is that only small signals are applied. Dowling et al. (1988) and Franklin et al. (1991b) demonstrated that the small signals required for EIS do not adversely affect the number and activity of microorganisms within a biofilm.

Several reports have been published in which EIS has been used to study the role of SRB in the corrosion of buried pipes (Kasahara and Kajiyama, 1986; King et al., 1986; Kasahara and Kajiyama, 1990) and reinforced concrete (Moosavi et al., 1986). Often EIS data were used only to determine the R_p defined as the dc limit of the real part of the impedance:

$$R_p = \lim_{f \to 0} \{Re(Z)\} - R_u ,\qquad(7)$$

where R_u is the solution resistance. This type of analysis is qualitative and no models for the impedance behavior have been presented for complicated systems encountered in MIC. Dowling et al. (1989) studied the effects of MIC on stainless steel weldments in artificial seawater using EIS and small amplitude cyclic voltametry. They concluded, from the frequency dependence of the impedance data, that two relaxations were associated with an as-welded inoculated surface, while only one time constant was detected in Bode-plots for an as-welded sterile surface or a polished surface of the same material. The authors speculated

Figure 6. Time dependence of the galvanic current in the presence of SRB Hase$^-$ (curve A) and SRB Hase+ (curve B) (Daumas et al., 1988).

that the occurrence of a second time constant was due to the development of pits. Dowling et al. (1988) used EIS to study the corrosion behavior of carbon steels affected by bacteria and determined R_p from EIS data. The majority of the impedance diagrams exhibited single depressed capacitive loop from which R_p was determined as the diameter of the loop. Under certain conditions, a second low-frequency capacitive loop was observed. However, no attempts were made to determine the significance of this second time constant. Dowling et al. (1988) were able to correlate the effects of certain experimental parameters including flow rate or type of bacteria with corrosion rates using EIS. White et al. (1990) determined the corrosion rate of steel in the presence of bacteria based on R_p data obtained from EIS. They suggested that EIS has an advantage for on-line, non-destructive monitoring of localized corrosion phenomena occurring in MIC. In an investigation of buried ductile iron pipes, Kasahara and Kajiyama (1990) concluded that EIS provided useful information in MIC testing, not only in terms of corrosion rates, but also mechanistic aspects.

The formation of biofilms and calcareous deposits on three stainless steels and titanium during exposure to natural seawater was followed using EIS and surface analysis with SEM/EDS (Mansfeld et al., 1990a, 1991b). Samples were either exposed at E_{corr} or polarized at –850 mV vs. SCE. Figure 7 is an example of data for unpolarized samples. The impedance is dominated by the capacitive component. No changes in the shape of the spectra were detected as the biofilm

Figure 8. Time dependence of the electrode capacitance C_{dl} for unpolarized stainless steels and titanium exposed to flowing natural seawater (Mansfeld et al., 1990a, 1991b).

formed with increasing exposure time. Figure 8 shows the time dependence of the electrode capacitance (C_{dl}) for the four materials. The average value of C_{dl} is close to the theoretical value for the double layer capacitance. Failure to detect a contribution of the biofilm to impedance spectra is probably due to its thickness of several tens of μm, which leads 'o a very small film capacitance and to the porosity of the water-like biofilm. The combination of these two effects makes it impossible to detect the formation of the biofilm in the experimental frequency range. No evidence of localized corrosion was observed for any of the samples by visual observation or microscopic examination over an exposure period exceeding four months. The impedance spectra also did not show any of the features which result from localized corrosion of stainless steels, such as the occurrence of a new time constant in the intermediate frequency region and a lowering of the dc limit corresponding to a lower R_p (Mansfeld and Little, 1991a). Impedance spectra for five copper-based materials exposed under the same conditions and in artificial seawater proved to be much more complicated than those for the stainless steels and titanium. The spectra changed with exposure time and reflected the effects of the formation of corrosion products and biofilms as well as mass transport (Little and Mansfeld, 1991).
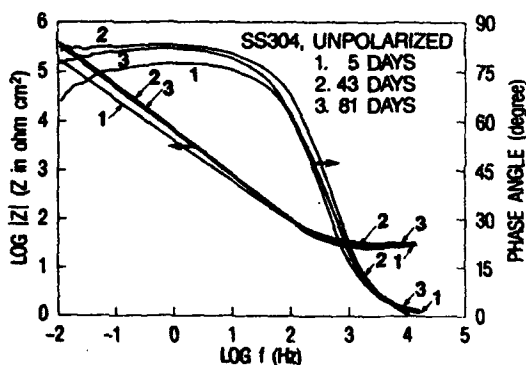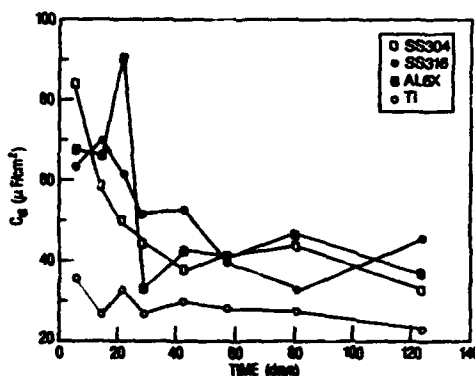
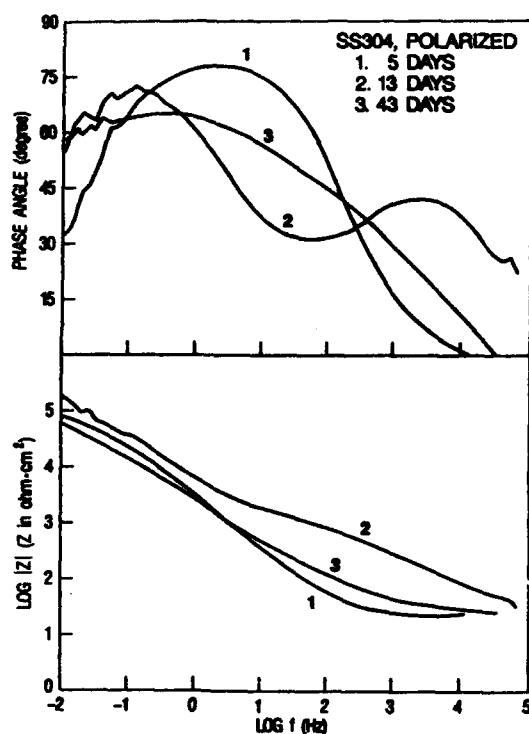Pronounced changes in impedance spectra were

Figure 7. Bode-plots as a function of exposure time for unpolarized SS304 exposed to flowing natural seawater (Mansfeld et al., 1990a, 1991b).

Figure 9. Bode-plots for SS304, polarized to –850 mV vs. SCE, as a function of exposure time to flowing natural seawater (Mansfeld et al., 1990a, 1991b).

Figure 10. Bode-plots for titanium, polarized to –850 mV vs. SCE, as a function of exposure time to flowing natural seawater (Mansfeld et al., 1990a, 1991b).

observed for polarized stainless steel and titanium samples exposed to natural seawater (Mansfeld et al., 1990a, 1991b). Figure 9 shows spectra at three exposure times for SS304. Similar data were obtained for SS316 and SSAL6X. At short exposure times one time constant was observed, similar to data for unpolarized samples. A second time constant appeared as a calcareous deposit formed. SEM analysis showed that the area not covered by the calcareous deposit was colonized by bacteria. When a dense calcareous deposit covered the entire surface, the time constant at the higher frequencies disappeared. Data for titanium after 43 days indicate the persistence of two time constants (Fig. 10). This behavior was explained by the different morphology of the calcareous deposit on titanium using the model for the impedance of a porous polymer film on metals (Mansfeld et al., 1982; Kendig et al., 1983).
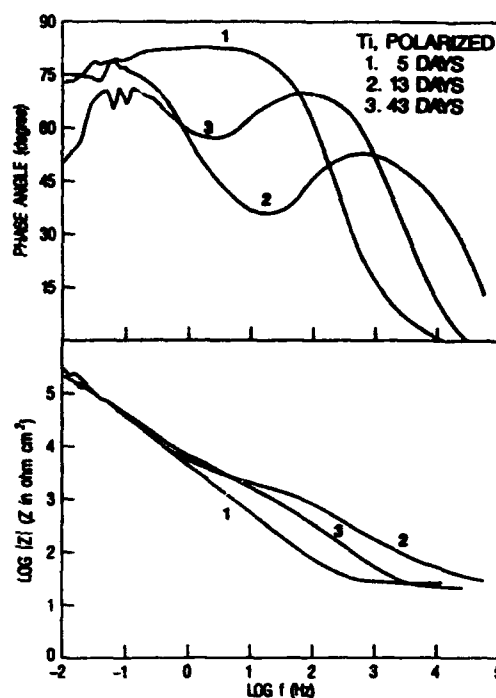
Ferrante and Feron (1990), using a combination of E_{corr} measurements and recording of polarization curves and EIS data, concluded that the material composition of steels containing 2–9% chromium and 1–10% molybdenum was more important for MIC resistance than bacterial population, incubation time, sulphide content, and other products of bacterial growth. EIS data showed a high-frequency time constant, which was attributed to biofilm formation (Fig. 11).

Jones et al. (1991) used EIS to determine the effects of several mixed microbiological communities on the protective properties of epoxy coatings on steel. EIS data were analyzed using a model for the impedance of polymer coated metals (Mansfeld et al., 1982; Kendig et al., 1983). In addition, a damage function was defined which allowed qualitative assessment of coating deterioration due to MIC.
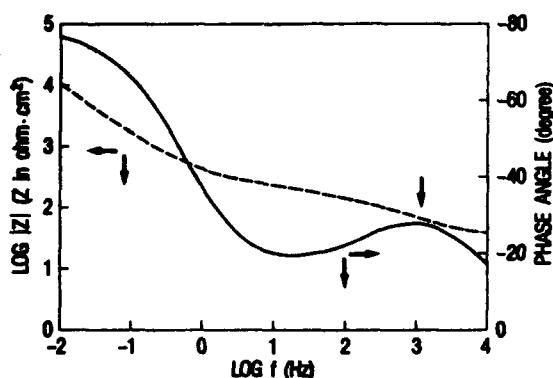
Figure 11. Bode-plots for an EM 12 steel electrode exposed to a batch culture of D. vulgaris for 500 h (Ferrante and Feron, 1990).
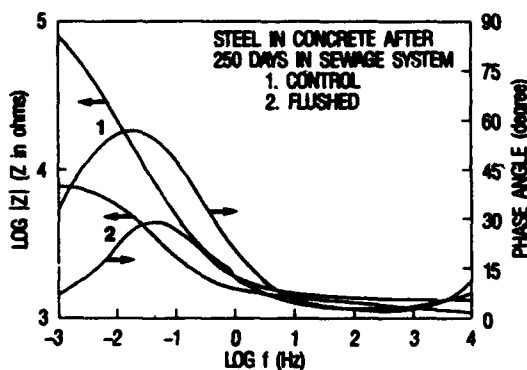

Figure 12. Bode-plots for mild steel embedded in concrete after 250 days exposure in a corrosion chamber fed with sewer gas; control (curve 1), flushed periodically with sewage (curve 2) (Mansfeld et al., 1990b, 1991a).

EIS measurements were also used to evaluate the corrosion behavior of steel sensors embedded in a concrete sewer bypass (Mansfeld et al., 1990b, 1991a) After tests had been terminated, EIS data were collected in the laboratory using a two-electrode system at $E_{appl} = 0$ mV. Analysis of the impedance spectra showed that R_p was lower for the mild steel sensors embedded in concrete samples flushed periodically with sewage (Fig. 12). This result is in agreement

with the R_p data derived from the linear polarization resistance technique shown in Figure 5 (Mansfeld et al., 1990b, 1991a).

Electrochemical Noise Analysis (ENA)

Electrochemical noise analyses follow fluctuations of potential, often E_{corr} or current, as a function of time or experimental conditions. One of the advantages of this technique is that no external signal needs to be applied. In some cases, the potential of a test electrode is measured versus a stable reference electrode (potential noise). In others, noise data are recorded for two electrodes of the same material connected to a ZRA (current noise). Recent studies show that the combination of potential and current noise data from the same two-electrode system provides significantly more information than the measurement of only one of these parameters (Kendig et al., 1988; Chen and Skerry, 1991). Analysis of the structure of the electrochemical noise data using the frequency dependence of the power spectral density can provide information concerning the nature of the corrosion processes and the magnitude of the corrosion rate.

Most electrochemical noise measurements applied to MIC have been of a qualitative nature with the goal to detect and monitor localized corrosion phenomena. Impedance and electrochemical noise measurements have been combined in a series of experiments designed to simulate conditions in concrete oil storage tanks (Moosavi et al., 1986). Electrochemical noise data obtained with a portable multichannel instrument, which also performed zero resistance ammetry, were converted to the frequency domain and subjected to a statistical analysis. Noise data collected at E_{corr} for a reinforced concrete block exposed to a marine medium containing active SRB were presented in a time record and a potential distribution chart showing the population and the magnitude of the potential fluctuations. Fluctuations in the noise record for 218 days were interpreted as being due to the sudden rupture of the protective oxide film followed by immediate repassivation. Events recorded for an exposed rebar showed fluctuations lower by a factor of 10 than those observed with a covered rebar. Since the magnitude of noise fluctuations depends on the total impedance of the system, it is possible that a corroding metal undergoing uniform corrosion with fairly high corrosion rates might be less noisy than a passive metal showing occasional bursts of noise due to localized breakdown of the film followed by rapid repassivation.

King et al. (1986) interpreted noise measurements for steel pipes in environments containing SRB as

being indicative of film formation and breakdown as the probable mechanism of corrosion. Iverson (1968a and b) conducted electrochemical noise measurements by capacitatively coupling a platinum electrode to the test specimen. Noise was measured across a resistor between the two electrodes. Since the test electrode was polarized to an unknown extent, any noise measured might be a result of polarization. Potential noise data were obtained in the laboratory for mild steel in a trypticase seawater culture of the marine strain of a marine SRB and in the field for a gas transmission line. It was concluded that breakdown of the iron sulfide film was accompanied by the generation of electrochemical noise.

Scanning Vibrating Electrode Techniques

The scanning vibrating electrode technique (SVET) provides a sensitive means of locating local anodic and cathodic currents associated with corrosion (Isaacs and Vyas, 1981). Franklin et al. (1991a) used auto-radiography of bacterial incorporated ^{14}C acetate to locate bacterial metabolic activity and a scanning vibrating electrode to define anodic and cathodic currents on colonized steel surfaces. Their results showed a correlation between the location of anodic activity of the steel and the location of incorporated radioactive label, suggesting that actively metabolizing bacteria may accelerate propagation of pits by colonizing active anodic sites. Franklin et al. (1990) used SVET and monitoring of E_{corr} to analyze the effects of microbial biofilms on inhibition of carbon steel corrosion by phosphate.

Large Signal Polarization Techniques

In the electrochemical techniques described above, measurements are carried out without the application of an external signal (E_{corr}, SVET, dual-cell technique, electrochemical noise), or with the application of only a very small perturbation (R_p, EIS). Large signal polarization techniques require potential scans ranging from several hundred mV to several V. Polarization curves provide an overview of reactions for a given corrosion system—charge transfer or diffusion controlled reactions, passivity, transpassivity, and localized corrosion phenomena. The effects of alloying or the addition of inhibitors can be recognized in the changes of the polarization curves. Quantitative information obtained from polarization curves includes the values of b_a and b_c, i_{corr}, the diffusion-limited current density for hydrogen reduction ($i_{1,H}$) and oxygen reduction (i_{1,O_2}), and parameters related to passivity, such as the critical potential (E_{crit}) and the critical current density (i_{crit}) for passivation, and the

passive current density (i_{pass}). Pitting potential (E_{pit}) and protection potential (E_{prot}) are related to the susceptibility of a metal for localized corrosion.

Numerous investigators have used polarization curves to determine the effects of microorganisms on the electrochemical properties of metal surfaces and the resulting corrosion behavior. In most of these studies comparisons have been made between polarization curves in sterile media with those obtained in the presence of bacteria and fungi. Early studies of MIC of mild steel were reviewed by Costello (1969). Horvarth (1961) was the first investigator using polarization techniques to study the acceleration of corrosion rates in the presence of SRB. Tiller (1986) reviewed the European research effort on microbial corrosion between 1950 and 1984. His paper contains 21 references to the use of polarization curves for the interpretation of the impact of SRB on mild steel. Duquette and Ricker (1986) reviewed polarization techniques applied to MIC.

The complexity of the reactions at a naval brass/polluted seawater interface was demonstrated by Deshmukh et al. (1988), who determined the influence of sulfide pollutants based on the results from potentiodynamic polarization curves. The shape of the anodic polarization curve changed drastically in the presence of sulfides or SRB (Fig. 13), and E_{corr} became substantially more negative. An active-passive transition and hysteresis in the reverse scan were observed. De Mele (1986) used polarization techniques to evaluate biodeterioration of implant materials, including aluminum in human plasma and silver in saline solution containing Na_2S. Feron (1990), in a
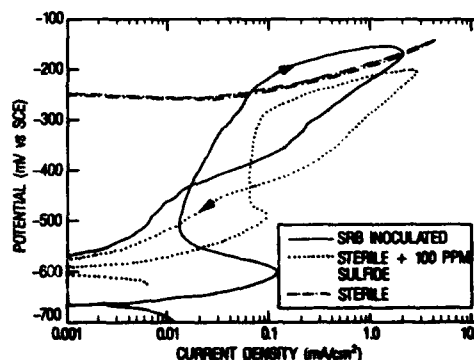
Figure 13. Potentiodynamic polarization curves for naval brass in seawater media (Deshmukh et al., 1988).

study of the corrosion behavior of austenitic and ferritic stainless steels in the presence of SRB, concluded that sulfides had a major influence on the passivity of these materials. Based on measurements of E_{corr}, EIS-data, and polarization curves, Feron (1990) suggested that although corrosion was more severe in the presence of SRB, the electrochemical reactions were the same as those observed in similar environments without bacteria.

Experimental evidence documents the drastic increase of corrosion rates of many structural materials caused by sulfides produced by microorganisms. In an attempt to quantify the effects of sulfides on the rates of the anodic and cathodic reactions of copper- and nickel-based materials, Mansfeld et al. (1992) added Na_2S to artificial seawater and measured the anodic polarization curves for five copper-based materials and pure nickel. As shown in Figure 14a for 99Cu, no significant changes of the polarization curves were observed for additions below 10 ppm. When 100 ppm Na_2S was added, E_{corr} showed a very large decrease and an anodic-limiting current was observed. Polarization curves with and without addition of sulfide coincided in the potential region anodic to E_{corr} in sulfide-free solutions. Similar results were obtained for 90Cu:10Ni, 70Cu:30Ni, admiralty brass, and aluminum bronze (Mansfeld et al., 1992). These results confirm the data presented by Deshmukh et al. (1988) (Fig. 13). Nickel was much more sensitive to additions of sulfide than the copper-based materials (Fig. 14b). In the presence of 10 ppm S^{2-}, a large increase of the anodic dissolution current density at a given potential was observed. This effect was even more pronounced in the presence of 100 ppm S^{2-}. The anodic dissolution rate at a potential equal to E_{corr} in the absence of S^{2-} increased by several orders of magnitude in the presence of S^{2-}. A qualitative analysis of the polarization curves in Figure 14b suggests that sulfides drastically increase rates of the anodic reaction of nickel exposed to seawater. For copper-based materials (Figs. 13 and 14a), sulfides added in sufficient amounts affect mainly the cathodic reaction. Results shown in Figure 14 might explain the intergranular corrosion observed for 70Cu:30Ni exposed to natural seawater, but not in artificial seawater (Mansfeld and Little, 1991b).

Polarization techniques have also been used to determine mechanisms by which microorganisms induce localized corrosion in the forms of pitting or crevice corrosion. In most cases, E_{pit} was determined

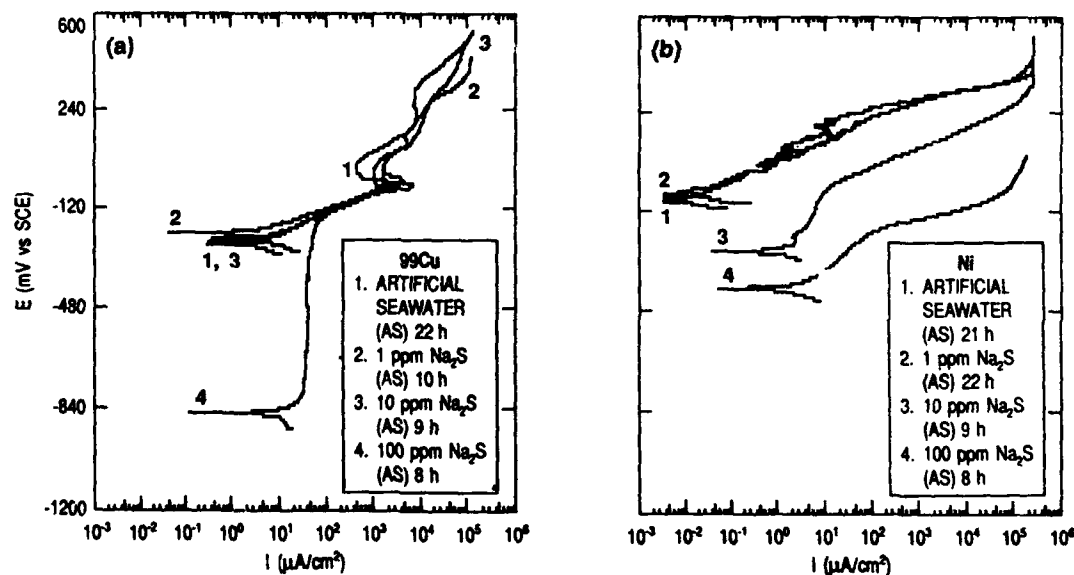Figure 14. Potentiodynamic polarization curves for (a) 99Cu and (b) pure nickel in artificial seawater as a function of Na_2S concentration (Mansfeld et al., 1992).

in the presence and absence of bacteria. However, E_{pit} provides data only for the tendency for pitting, but not for the rate of pit propagation. The extent of pitting in the presence of biofilms cannot be predicted based on E_{pit} alone. Salvarezza et al. (1979) and De Mele et al. (1979) used microbial isolates obtained from jet fuel storage tank sludges to determine the influence of microorganisms on corrosion of aluminum alloys in fuel-water systems. They concluded that E_{pit} could be used to determine biological attack. Rosales and DeSchiapparelli (1980), Rosales (1986), DeSchiapparelli and Rosales (1980), and Allyon and Rosales (1988) determined the influence of microbial contaminants in aircraft fuel, alloying elements, and surface heterogeneities on initiation and propagation of pitting in aluminum 7075 and concluded that electrochemical tests reproduced the corrosion problems observed in service conditions.

Ringas and Robinson (1988) performed electrochemical tests on stainless steels and mild steels in three cultures of SRB. In all cases the pitting resistance was lower in cultures of SRB. Figure 15 shows potentiodynamic polarization curves with a reverse scan for SS316 in sterile media and in cultures of SRB. In sterile media, the alloy was passive and displayed a large passive range. The reverse sca., showed that active pits did not form. The shape of the anodic polarization curve was very different in the bacterial culture. E_{corr} was more active—an active-passive transition was observed and i_{pass} was

Figure 15. Pitting scans for SS316 in sterile medium and strain 8303 (Ringas and Robinson, 1988).

higher—suggesting that the passive film formed in the bacterial culture was less protective. The reverse scan showed that active pits had been formed and did not repassivate. Similar results were reported by Ringas and Robinson (1988) for SS409 and 430. The authors concluded that sulfide-induced pits were initiated at more negative potentials than those initiated by chlorides. Salvago et al. (1990) obtained cathodic polarization curves for SS254 SMO coupled to zinc, iron, tin, cadmium, brass, copper-nickel alloys, molybdenum, and stainless steels. They concluded that such studies are particularly useful for monitoring biofilms formed in natural seawater. Licina and Nekoksa (1990) suggested that monitoring current at an applied potential of -400 mV to -600 mV vs. SCE could be used to follow the growth of biofilms on stainless steels in fresh water. As previously discussed, the rate of the cathodic reduction reaction can increase with time for stainless steels as the biofilm forms.

Hydrogen Permeation Techniques

Since bacteria produce copious amounts of hydrogen and acids as metabolic by-products during growth on metal surfaces, and since sulfide acts as a hydrogen recombination poison, it is possible that bacteria can contribute to environmental cracking on stressed metals. Ford and Mitchell (1990) and Walch et al. (1989) used a variation of the electrochemical hydrogen permeation technique (Devanathan and Stachurski, 1962) to study environmental cracking under biofilms. They concluded that hydrogen, acid, and sulfide production by bacteria may significantly contribute to environmental cracking of susceptible materials.

SUMMARY AND CONCLUSIONS

This review of the use of electrochemical techniques in studies of MIC demonstrates the increasing attention that MIC is receiving in the corrosion community. Of the 90 papers reviewed, 62 have been published since 1986. So far, electrochemical techniques have been used mainly to demonstrate that MIC can happen for a large number of materials in a large number of environments. Often, corrosion rates as determined from dc or ac techniques via the polarization resistance have been compared for abiotic and biotic environments. While this approach has increased the general knowledge base concerning the occurrence of MIC under a variety of circumstances, not much mechanistic information has been obtained. The central question of whether bacteria merely accelerate the anodic and cathodic partial reactions which determine the corrosion process, or whether new reaction paths occur,
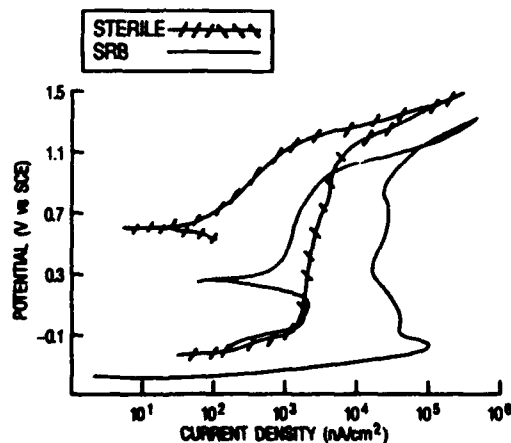
has seldom been investigated. It is interesting to note that the possibility of the inhibition of corrosion due to microbial activity has apparently not been considered. As pointed out in the Introduction of this review, it seems probable that reactions such as the direct reduction of H_2S can occur in MIC; however, few authors have addressed this point in the design of their experimental approach. The role of sulfides as corrosion products and their activity in the reduction of oxygen seems to be one of the most important aspects for the explanation of MIC of steels. The corrosion behavior of structural materials in the presence of organic acids and the role of oxygen under these circumstances is poorly understood and needs more attention. The entire range of environmental cracking of structural materials due to MIC has received very little attention.

Ennoblement of E_{corr} for stainless steels, reported by some authors, remains a subject for which no satisfactory mechanism has been demonstrated. Obviously the environmental chemistry which determines the composition and activity of a biofilm and the local chemistry under the biofilm determine the degree of ennoblement. Experimental evidence suggests that ennoblement of E_{corr} is due to an increase of the rate of the cathodic reaction. However, the mechanism for this phenomenon remains unclear mainly due to the fact that the experimental evidence consists only of measurements of E_{corr} and/or the cathodic current at a potential more negative than E_{corr}. Progress can only be made if surface analytical techniques are applied to samples for which ennoblement has been observed to determine whether changes in the properties of the passive film are the cause of ennoblement, or whether compounds deposited on the passive surface in contact with the biofilm act as catalysts to accelerate the rate of the cathodic reaction. Considering the complicated nature of an "aged" surface covered by a biofilm, such analyses might be quite complicated.

Most corrosion reactions in MIC are of a very localized nature. This fact makes the use of electrochemical techniques, which in general produce an average signal over the entire surface, difficult. In this respect, the use of electrochemical techniques in the evaluation of MIC is limited to the same degree as all studies of localized corrosion phenomena. Combinations of EIS, ENA, and pit propagation rates as determined by the thin foil technique suggested by Boehni (1987) seem to be very promising. The use of microsensors for the determination of local chemistries under the biofilm and the various potential or current scanning techniques discussed in this review should provide additional material for mechanistic

interpretation.

In an area of corrosion as complicated as MIC, one single class of experimental techniques cannot be expected to provide all the answers needed for the establishment of mechanisms of MIC. As in other fields of corrosion, input is needed from complimentary disciplines including surface analytical techniques and microbiological techniques.

ACKNOWLEDGMENT

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